



English Translation of JP 56-103131

Japanese Patent Application No. 55-5261, filed January 22, 1980

Japanese Patent Application Laying open (KOKAI) No. 56-103131,  
published August 18, 1981

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**Specification**

1. Title of the Invention

METHOD OF PREPARING CARBOXYLIC ACID CHLORIDE

2. Claims

1. A method of preparing a carboxylic acid chloride, comprising reacting an organic carboxylic acid or a carboxylic anhydride thereof with phosgene in the presence of a catalyst to prepare a corresponding carboxylic acid chloride, wherein almost to an end point of the reaction, the phosgene is supplied at such a rate that unreacted phosgene is not substantially detected in an exhaust gas.

2. The method according to claim 1, wherein the organic carboxylic acid is a carboxylic acid having an even number of carboxyl groups present at such positions that the carboxyl groups are bonded with each other to form an anhydride in a molecule.

3. Detailed Description of the Invention

The present invention relates to a method of preparing a carboxylic acid chloride, and further an improved method of preparing a carboxylic acid chloride, which includes reacting an organic carboxylic acid or a carboxylic anhydride thereof with phosgene in the presence of a catalyst to prepare a

corresponding carboxylic acid chloride with high yield and high quality.

In recent years, carboxylic acid chlorides become industrially important as a starting material for heat-resistant resins, pharmaceutical medicines, pesticides, or the like.

As such a method of preparing this kind of carboxylic acid chloride, there is generally a method of chlorinating a carboxylic acid with thionyl chloride, phosphorus pentachloride, phosphoryl chloride, or the like. However, since these chlorinating agents are expensive, and the treatment of byproducts becomes a problem, the preparation by this method in an industrial scale accompanies various disadvantages and difficulties.

Although the method using phosgene was known formerly, phosgene gives poor reactivity than the above chlorinating agents, and this method requires use of a catalyst. In recent years, there were proposed as the catalyst, compounds such as dimethylformamide (Japanese Patent Application Publication No. 43-10613), quaternary ammonium salt and phosphonium salt (Japanese Patent Application Publication No. 44-27363), tetraalkylthiourea (Japanese Patent Application Publication No. 44-27362), imidazole (Japanese Patent Application Publication No. 47-13021), or trimethylphosphine oxide (Japanese Patent Application Laid-Open No. 50-30821). Particularly, as a catalyst which has high activity and is inexpensively available, there are generally lower aliphatic amides such as dimethylformamide.

While using these catalysts, many carboxylic acids or carboxylic anhydrides are reacted with phosgene to usually obtain corresponding carboxylic acid chlorides with high yield and high quality.

However, when a certain carboxylic acid such as phthalic acid or phthalic anhydride is reacted with phosgene in the presence of the above-described and known catalyst, the yield of the obtained corresponding carboxylic acid chloride is no more than remarkably low yield. For example, according to the method disclosed in the specification of U. S. Patent No. 3,810,940, the reaction of phthalic anhydride and phosgene using dimethylformamide as a catalyst is performed in a monochlorobenzene solvent to obtain phthalic acid chloride with the yield of 71.6%. Also, in the case of performing the same method in hexane solvent, it is reported that the compound of interest was not obtained (the specification of U. S. Patent No. 3,318,950).

The present inventors earnestly studied on the cause of the low yield in the method of the above-described U. S. patent. Finally, it was found that in the case of a large phosgene-supplying rate, a catalyst becomes a tar-like product from the initial stage of the reaction to lose catalytic activity, whereby the reaction does not proceed. Accordingly, the present inventors have accomplished the present invention by finding that an industrially simple method of controlling the supply rate of phosgene, in which phosgene is supplied at such a rate that unreacted phosgene is not substantially detected in an

exhaust gas almost to the end point of the reaction, makes it possible to obtain the corresponding carboxylic acid chloride with high yield and high quality.

As the method of detecting the unreacted phosgene in the exhaust gas, any method may be employed, and for example, the detection is easily confirmed by directly measuring the exhaust gas with gas chromatography.

Any known carboxylic acid or anhydride thereof may be used, but the carboxylic acid or anhydride thereof which shows the advantage of the present invention most remarkably is a carboxylic acid or anhydride thereof which has an even number of carboxyl groups present at such positions that carboxyl groups are bonded with each other to form an anhydride in a molecule, such as phthalic acid, tetrahydrophthalic acid, or anhydrides thereof, succinic acid, maleic acid, or anhydrides thereof in which a carboxylic acid chloride with only low yield has been conventionally obtained by phosgenation.

Although one of the known catalysts as described above can be used as the catalyst, quaternary ammonium salt or tetraalkylthiourea has a small catalytic activity and is not practical, and trimethylphosphine oxide is expensive. But, the use of a lower aliphatic amide such as imidazole or dimethylformamide, which is relatively inexpensive and has a high catalytic activity, is preferable.

It is preferable that the amount of the catalyst is 0.01 moles or more, particularly 0.05 to 0.1 mol based on 1 mol of carboxylic acid. If an amount larger than this range is used,

the reaction rate does not become very high, and only a tar-like compound is formed, whereby the effect is small.

It is preferable that the operation temperature range is 50° to 120°C, particularly 70° to 90°C. At a temperature lower than this range, the reaction rate becomes low, and at a temperature larger than this range, the formation rate of the tar-like compound becomes remarkably high.

The reaction can be performed in the presence or absence of a solvent. Any known solvent can be used as the solvent used herein. The use of aliphatic hydrocarbon such as hexane or heptane makes the reaction time long and is not practical. As examples of solvent, hydrocarbons such as benzene, toluene, xylene, monochlorobenzene and dichlorobenzene, and oxygen-containing compounds such as ether and tetrahydrofuran are practically listed.

Next, examples of the present invention are described.

#### Example 1

2.6 g (0.035 mol) of dimethylformamide as a catalyst, 74.1 g (0.50 mol) of phthalic anhydride, and 74.1g of toluene were charged in a 300-ml four-necked flask equipped with a stirrer, a gas-introducing pipe, a thermometer and a Dimroth condenser. While stirring, phosgene was blown at the rate of 7 g/hour into the flask and the reaction was performed at 70°C for 10 hours. During this time, the detection of unreacted phosgene was started from the time of the conversion rate of about 90%.

After completing the reaction, a catalyst layer separated to a lower layer was divided as a solution, and then toluene

was removed off from the reaction solution under reduced pressure.

Successively, the reaction solution was distilled to obtain 100.5 g of a fraction having a boiling point of 151° to 154°C/20 mmHg (crude yield of 99.0%). The obtained o-phthalic acid chloride had a purity of 99.4% and contained 0.4% of unreacted phthalic anhydride.

#### Comparative Example 1

The same reaction as in Example 1 was performed except that the supply rate of phosgene was changed to 11 g/hour. During this reaction, the unreacted phosgene was detected in an exhaust gas from the time of a conversion rate of about 50%, and the reaction stopped after the elapse of 7 hours.

The same treatment as in Example 1 was performed to obtain 99.8g of a fraction containing o-phthalic acid chloride. This fraction contained 85% of o-phthalic acid chloride, and the other was unreacted phthalic anhydride.

#### Comparative example 2

The same reaction as in Example 1 was performed except that the reaction temperature was changed to 100 °C and the phosgene-supplying rate was changed to 14 g/hour. During this reaction, the unreacted phosgene was detected in an exhaust gas from the initial stage of the reaction, and the reaction did not proceed at the time of the conversion of about 50% after the elapse of 4 hours from the start of the reaction.

The same treatment as in Example 1 was performed to obtain 100.0 g of a fraction. This fraction contained 52% of o-phthalic

acid chloride, and the other was unreacted phthalic anhydride.

#### Example 2

The same reaction as in Example 1 was performed except that o-dichlorobenzene was used in place of toluene. The reaction was completed after the elapse of 11 hours.

After completing the reaction, a catalyst layer separated to an upper layer was divided as a solution, and then the reaction solution was treated in the same manner as in Example 1 to obtain 100.2 g of a fraction (crude yield of 98.7%). The obtained o-phthalic acid chloride had a purity of 99.1% and contained 0.7% of unreacted phthalic anhydride.

#### Example 3

50.0 g (0.5 mol) of succinic anhydride, 50 g of toluene and 2.6 g (0.035 mol) dimethylformamide were charged in a 200-ml reactor equipped with the devices as described in Example 1. While stirring, phosgene was blown at the rate of 10 g/hour into the reactor and the reaction was performed at 70°C for 6 hours. During this time, the detection of unreacted phosgene was started from the time of the conversion rate of about 90%.

After completing the reaction, a catalyst layer separated to an upper layer was divided as a solution, and the reaction solution was distilled under reduced pressure to obtain 76.7 g of succinic acid chloride (crude yield of 99.0%). Obtained succinic acid chloride had a purity of 99.8%.